AB INITIO R-MATRIX CALCULATIONS OF e^+ – MOLECULE SCATTERING

Grahame Danby and Jonathan Tennyson,
Department of Physics and Astronomy, University College London,
Gower St., London WC1E 6BT, England

ABSTRACT

The adaptation of the molecular R-matrix method, originally developed for electron–molecule collision studies, to positron scattering is discussed. *Ab initio* R-matrix calculations are presented for collisions of low-energy positrons with a number of diatomic systems including H_2, HF and N_2. Differential elastic cross-sections for e^+–H_2 show a minimum at about 45° for collision energies between 0.3 and 0.5 Ryd. Our calculations predict a bound state of e^+HF. Calculations on inelastic processes in N_2 and O_2 are also discussed.

INTRODUCTION

The first principles calculation of low-energy positron molecule collision parameters is an active area which has recently been reviewed by Armour[1]. The most accurate calculations have largely been confined to hydrogenic targets. Over the past few years we have been studying positron collisions from a variety of diatomic targets[2-7]. As we will show, these calculations have now reached the stage where they not only aim to reproduce experiment but have made a number of experimentally testable predictions.

METHOD

The R-matrix method has been successfully used for a number of years by Burke, Noble and co-workers to study low-energy electron molecule collisions, see Gillan *et al* [8] for a recent presentation of the theory. These calculations have been able to reproduce even subtle features of observed electron-molecule collisions.

The basis of the R-matrix method is the division of space into two regions. The internal region is contained in a sphere centred on the target molecule

centre-of-mass. This sphere is assumed to entirely enclose the target charge distribution. Typically, and for all calculations discussed below, the sphere has a radius of 10 a_0.

For positron–molecule collisions, the potential in the internal region comprises the repulsive positron – nuclei terms and the attractive, multicentre positron–electron interaction. The latter is particularly difficult to represent accurately. In the external region, the potential has a simple multipolar form representing the static moments of charge distribution and the dipole polarisability of the target.

An advantage of the R-matrix method is that computations on the difficult internal region are performed independent of scattering energy. This is done because the finite sphere has the effect of discretising the continuum which is then represented by numerical functions. These functions in principle form a complete set but in practice are truncated at some collision energy 2–3 times the highest energy of interest. The numerical functions augment L^2 functions, Slater Type Orbitals, which are used represent the target and to carry short range polarisation effects.

The R-matrix method of electron–molecule scattering has been extended to allow parallel studies for positron impact. Modifications consists of altering the signs of the relevant Coulomb integrals, neglecting exchange with target electrons and allowing the positron to occupy filled electron spinorbitals. In the internal region short and intermediate range polarisation effects are treated, respectively, by allowing single electron excitations of the target and by the introduction of polarised pseudostates. The asymptotic form of the polarisation potential is adopted for the outer region. Details of the implementation

of the R-matrix method for positron scattering calculations can be found in refs. 2 and 6.

RESULTS

Hydrogen molecule

Positron–H_2 calculations have been the subject of a series of studies by Armour and co-workers[1]. The best of these calculations are of high accuracy using explicit functions of the $e^- - e^+$ coordinates, so called Hylleraas functions, to give a good representation of electron–positron correlation, usually described as target polarisation effects. These calculations form a benchmark against which other methods can be tested.

We have recently completed a study of low-energy e^+–H_2 collisions[6]. These calculations tested several target representations, the best being one which recovered about 90% of the H_2 correlation energy. Methods of including short-, long- and intermediate-range polarisation effects were studied. These calculations showed that our short-range polarisation was not sufficient for the lowest Σ_g^+ symmetry but gave a good representation of higher symmetries. This enabled us to calculate differential cross sections for elastic e^+-H_2 collisions, an example of which is given below.
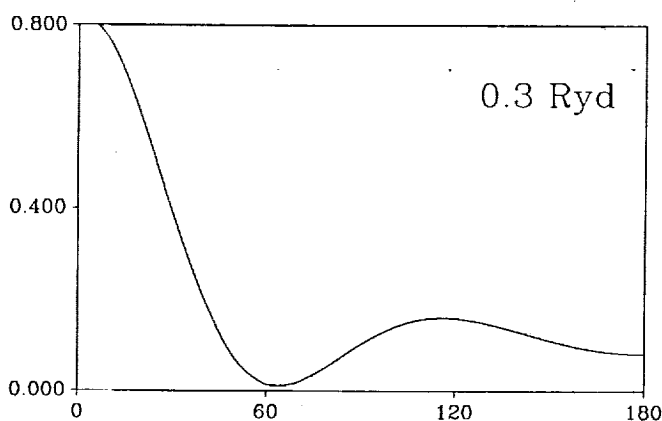

Fig. 1 Differential cross section, in a_0^2 sr^{-1}, for e^+–H_2 collisions[6].

These differential cross sections are of interest because they show a pronounced structure with a minimum in the cross section for all but the lowest energies. For scattering energies above 0.3 Ryd and below the positronium formation threshold this minimum is in the 40° – 60° region. Such minima have been predicted for e^+ - Noble gas systems but have

yet to be confirmed experimentally.

Hydrogen fluoride

The collisions of low-energy electrons with polar molecules have caused considerable recent interest because of the observation of sharp spikes, particularly in vibrational excitation cross sections, for a number of these systems. It is now generally accepted that these spikes are caused by resonances associated with ro-vibrationally excited states of a very weakly bound negative ion of the system in question. A well studied[9] example of such systems is e^-–HF.

Of course for positron scattering any corresponding series of resonances would have immediate consequences for positron annihilation rates. A number of systems have been observed to have unusually high values of Z_{eff} [10], several of which are molecules with a large dipole moment. R-matrix positron scattering calculations on HF do indeed reveal the presence of a weakly bound state[5].
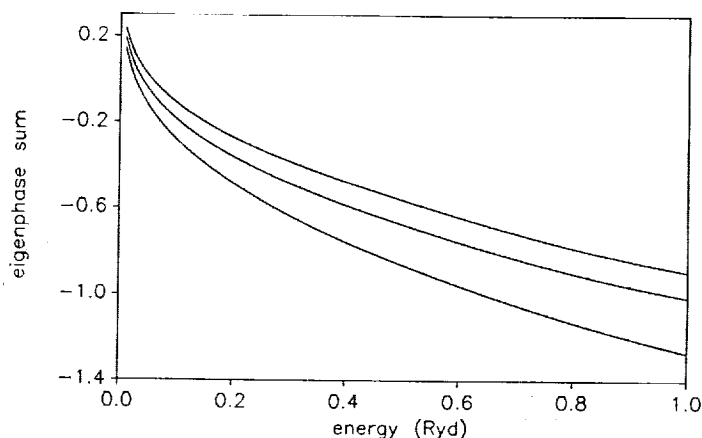

Fig. 2 Eigenphase sums for e^+-HF scattering with Σ_g^+ symmetry as a function of the degree of polarisation included in the calculation.

Since the publication of these calculations a programming error in our code has come to light[6]. This error only affects the inclusion of short range polarisation in our calculations and does not alter our conclusion that the e^+HF system supports a bound state. Above we give corrected eigenphase sums for scattering at the equilibrium HF geometry of 1.733 a_0. These eigenphase sums are, in order of increasing value, for static, static plus Σ polarisation and static plus Σ and Π polarisation models. These models are

analogous to those of Danby and Tennyson (1988).

For all models the HF eigenphase sums show a pronounced threshold peak characteristic of the presence of a bound state. Confirmation of a bound state can be obtained by searching the complex k plane to find a pole in the S-matrix (Morgan and Burke 1988). This analysis showed e^+HF to be bound by 1.4×10^{-9} Ryd in the static model and 3.1×10^{-9} Ryd in the $\Sigma + \Pi$ polarisation model. Adding further polarisation increases the binding energy to 3.3×10^{-9} Ryd.

Other systems

Calculations have been performed for scattering off a number of other diatomic targets such $CO^{3,4}$, $N_2{}^{2,4,7}$ and F_2. These calculations have explored not only elastic effects, such as those discussed above, but also inelastic processes. The $e^+ - CO$ calculations considered rotational excitation. Studies of vibrational excitation of N_2, of importance for the thermalisation of positrons in air, are nearing completion. Finally we have embarked on a study of electronic excitation effects in $e^+ - O_2$ collisions, a system for which unusual phenomena have already been observed experimentally[11].

CONCLUSIONS

Several positron – diatom collision systems have now been studied using the R-matrix method. These calculations have been shown to be capable of making firm predictions that are experimentally verifiable. It is clear that the calculations suffer from a weakness in that they uniformly underestimate the contribution due to the correlated positron – electron motions. This short range polarisation effect is most important at very low energies and for the penetrating s wave. Comparisons with H_2 calculations suggest that our calculations on symmetries higher than Σ_g^+ are not sensitive to this omission.

None of the calculations presented here made allowance for a positronium exit channel. This means that their range of validity is restricted to below the positronium formation threshold which occurs at a few eV for most molecules. Extension of our calculations into this region presents a formidable challenge, but one which is ripe for a concerted attempt to tackle.

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